Chapter 45 - **SANS FROM IONIC MICELLES**

Ionic micelles use surfactants with charged head groups. When mixed with hydrophilic and hydrophobic molecules, these self-assemble into micelles of various shapes. Micelles form in order to screen the hydrophobic groups and avoid their contact with water. Coulomb interactions contribute to micelle formation. A system that forms rodlike ionic micelles is described here.

1. AN IONIC RODLIKE MICELLES SYSTEM

Consider the following ionic micellar system: cationic surfactant cetyltrimethyl ammonium 4-vinylbenzoate (CTVB) in aqueous (d-water) solution (Kline, 1999; Kim et al, 2006). These form rodlike micelles. Free radical polymerization is performed on the VB groups in order to obtain polymerized micelles. After polymerization, negative charges (VB^-) are on the outer surface and positive charges (CTA^+) are on the inner surface of the rodlike polymerized micelles.

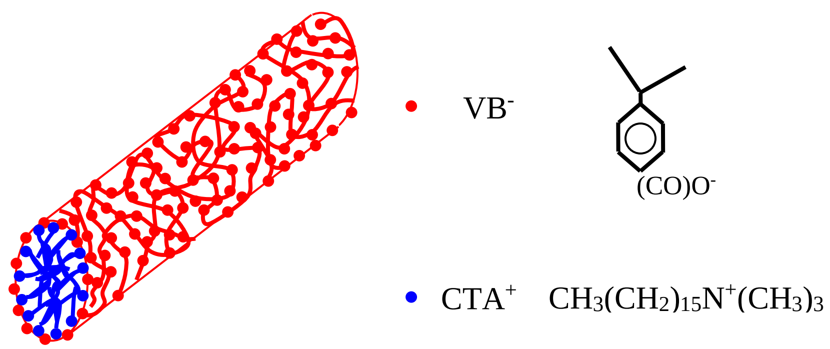

Figure 1: Schematic representation of the CTVB polymerized rodlike micelle.

A set of four CTVB/d-water samples were prepared with different micelles fractions. These correspond to 0.25 %, 0.5 %, 1 % and 1.9 % CTVB mass fractions. SANS measurements were made at 25 ^oC. As the mass fraction increases, an inter-particle “interaction” peak is seen to develop.

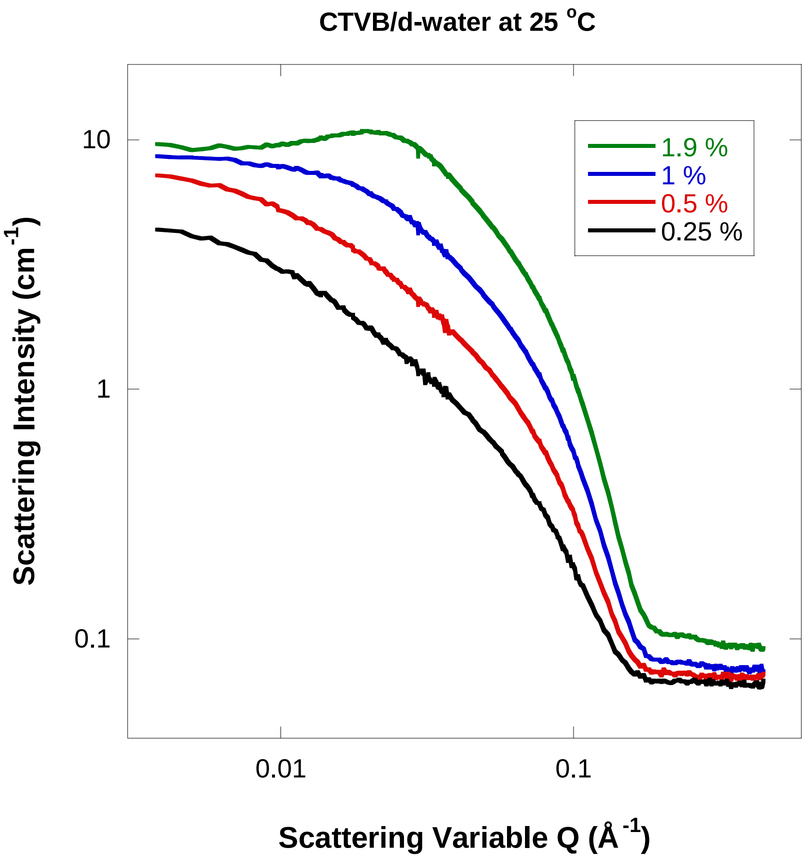

Figure 2: SANS data from CTVB/d-water for increasing concentration.

2. SCATTERING MODEL

A scattering model consisting of a solution of interacting rodlike particles is used to fit the SANS data. The scattering intensity (cross section) is given by:

$$I(Q) = \frac{d\Sigma(Q)}{d\Omega} + B = \Delta\rho^2 \phi V_P P(Q) S_I(Q) + B. \qquad (1)$$

Here $\Delta\rho^2$ is the contrast factor, ϕ is the particles volume fraction, V_P is the particle volume and B is a constant used to represent the Q-independent (mostly incoherent scattering) background.

The form factor for a cylinder is given by the following orientational average:

$$P(Q) = \frac{1}{2}\int_{-1}^{1} d\mu \, |F(Q,\mu)|^2. \qquad (2)$$

$$F(Q,\mu)=\left[\frac{\sin(Q\mu L/2)}{Q\mu L/2}\right]\left[\frac{2J_1(Q\sqrt{1-\mu^2}R)}{Q\sqrt{1-\mu^2}R}\right]. \qquad (3)$$

μ represents the rod orientation with respect to the scattering vector direction. R is the cylinder radius and L is its length. J_1 is the cylindrical Bessel function.

The structure factor for a solution of charged particles is obtained from the Ornstein-Zernike (OZ) equation solved with the Mean Spherical Approximation (MSA) closure relation. The MSA approach was used to account for the Coulomb interactions. Note that the MSA solution was originally introduced for spherical particles. Since there is no simple analytical approach that can model the structure factor for rodlike particles, the MSA is used here for lack of a better model. The structure factor is given by:

$$S_I(Q)=\frac{1}{1-\overline{N}C(K)} \qquad (4)$$

$$\begin{aligned}\frac{\overline{N}C(K)}{24\phi}&=\frac{A(\sin(K)-K\cos(K))}{K^3}+\frac{B\left[\left(\frac{2}{K^2}-1\right)K\cos(K)+2\sin(K)-\frac{2}{K}\right]}{K^3}\\&+\frac{\phi A\left[\frac{24}{K^3}+4\left(1-\frac{6}{K^2}\right)\sin(K)-\left(1-\frac{12}{K^2}+\frac{24}{K^4}\right)K\cos(K)\right]}{2K^3}\\&+\frac{C(k\cosh(k)\sin(K)-K\sinh(k)\cos(K))}{K(K^2+k^2)}\\&+\frac{F[k\sinh(k)\sin(K)-K(\cosh(k)\cos(K)-1)]}{K(K^2+k^2)}\\&+\frac{F(\cos(K)-1)}{K^2}-\frac{\gamma\exp(-k)(k\sin(K)+K\cos(K))}{K(K^2+k^2)}.\end{aligned}$$

Here K = QD is the reduced scattering variable and D is the rodlike micelle diameter.

Note that it is difficult to model overlapping rods since these could form liquid crystalline (such as nematic or smectic) phases. Only the isotropic phase (obtained for a low concentration of rods) can be modeled by the MSA approach and is of interest here.

Figure 3: Schematic representation of the main liquid crystal phases for rodlike particles. These are the isotropic, nematic and smectic phases obtained when the rodlike particle concentration increases.

3. FITS OF THE SANS DATA

Fits of the model to the SANS data are performed. Results for the 1 % mass fraction sample are included here. The contrast factor for the CTVB/d-water mixture was fixed as well as the dielectric constant ε and the sample temperature T.

$$\Delta\rho = \rho_{d\text{-water}} - \rho_{CTVB} = 6.39*10^{-6} - 0.35*10^{-6} = 6.04*10^{-6}\ Å^{-2} \quad (5)$$
$$\varepsilon = 77.94$$
$$T = 298\ K.$$

The remaining fitting parameters were varied and found to be:

$$\phi = 0.01 \quad (6)$$
$$R = 20.9\ Å$$
$$L = 184\ Å$$
$$z_m = 0.06$$
$$B = 0.074\ cm^{-1}.$$

In order to appreciate the contributions from the form factor and the structure factor terms, SANS data are compared to the results of the model fits in the dilute limit (i.e., when $S_I(Q)$=1). The structure factor $S_I(Q)$ is also plotted. The effect of inter-particle interactions is small but finite.

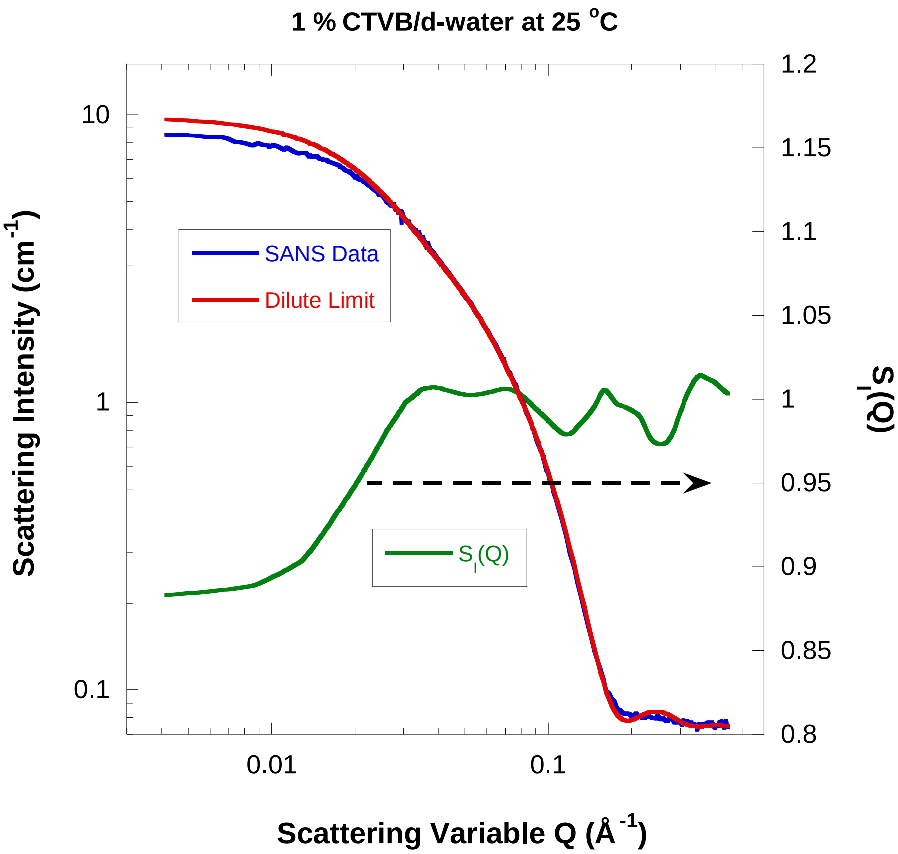

Figure 4: Comparison of the SANS data to the model fit in the dilute limit. The structure factor $S_I(Q)$ is also plotted.

The apparent radius of gyration for the rodlike cylinders of radius R and length L is calculated using:

$$R_g = \sqrt{\frac{R^2}{2} + \frac{L^2}{12}}. \qquad (7)$$

Results are plotted for increasing CTVB mass fraction. A polynomial fit is performed and yields:

$$\left(R_g\right)_{app} = \left(R_g\right)_0 - m_1\phi + m_2\phi^2 + \qquad (8)$$

This is sometime referred as a "virial expansion". The "real" radius of gyration is obtained at the infinite dilution limit as:

$$\left(R_g\right)_0 = 124\ \text{Å}. \qquad (9)$$

Note that the first dominant correction term in the expansion is negative. In the infinite dilution (subscript ID) limit, P(Q) decreases (and therefore R_g decreases) with increasing micelles fraction.

$$\frac{\left(\frac{d\Sigma(Q)}{d\Omega}\right)_{ID} - B}{\phi} = \Delta\rho^2 V_P P(Q) \,. \qquad (10)$$

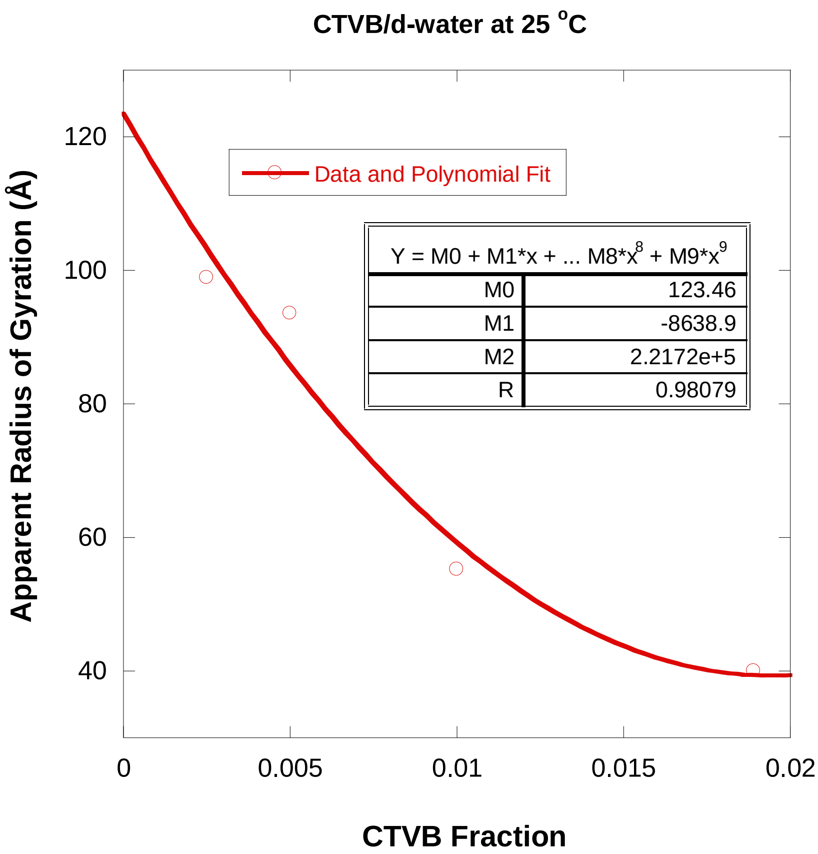

Figure 5: Variation of the apparent radius of gyration for increasing CTVB fraction.

Temperature was varied for the 1 % CTVB/d-water sample. Rodlike particle dimensions (R and L) were obtained from the fits. Since the micelles are polymerized, there is very weak (to non-existent) temperature dependence of the radius R but noticeable temperature dependence of the rod length L.

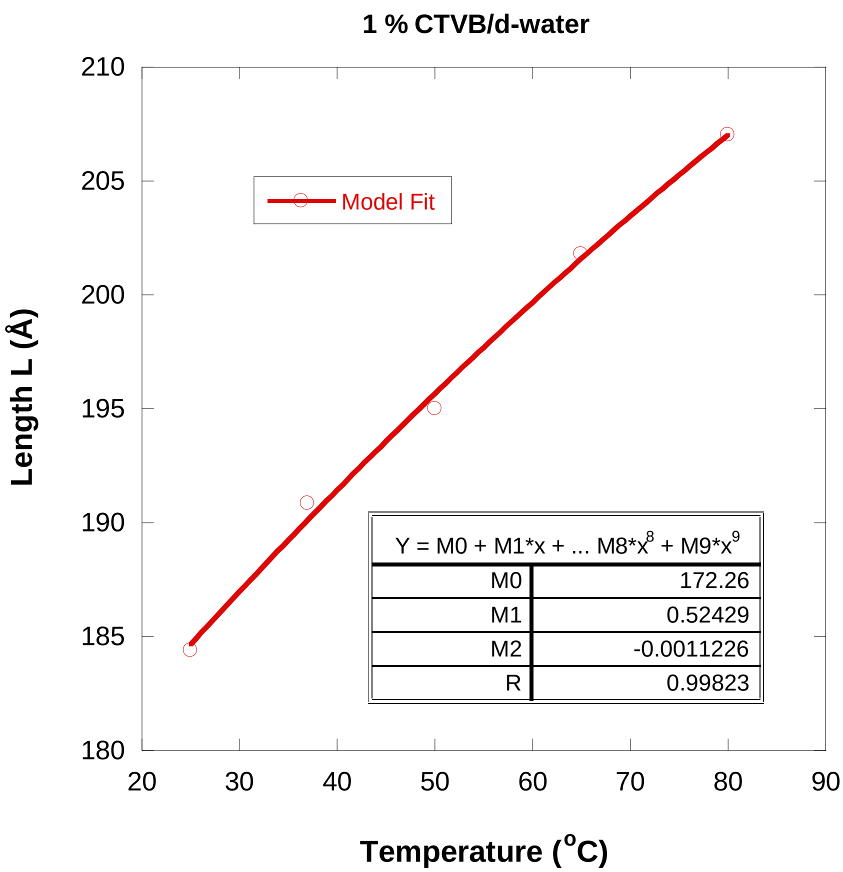

Figure 6: Temperature dependence of the rodlike particles length for increasing sample temperature.

In order to perform the fits to the SANS data when sample temperature was varied, temperature dependence of the dielectric constant for d-water was required. ε is seen to decrease with temperature as tabulated (CRC Handbook, 1984).

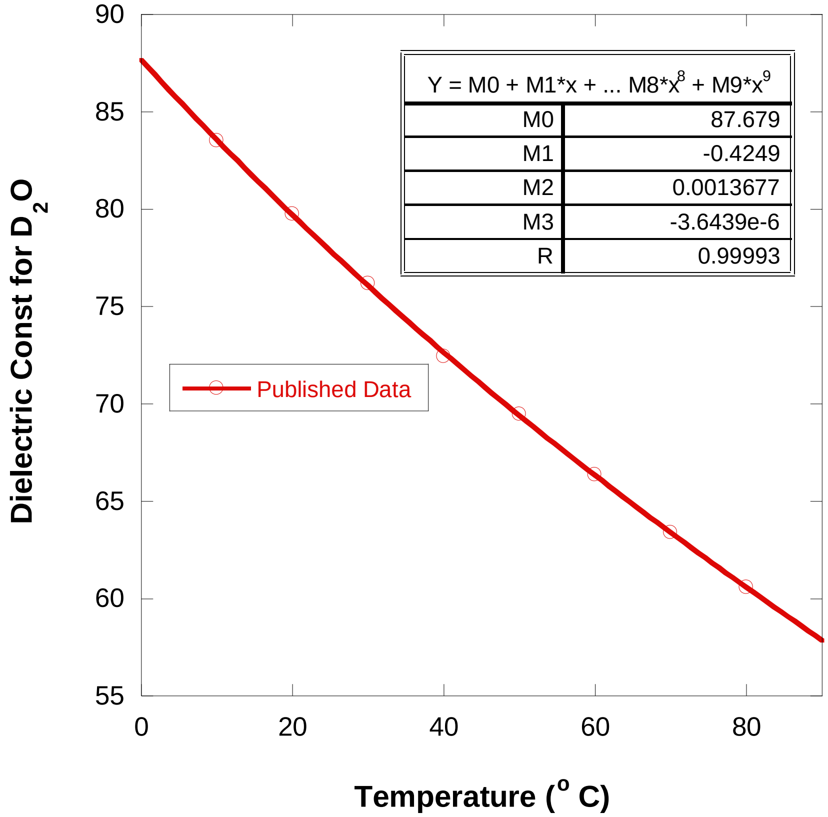

Figure 7: Temperature dependence of the dielectric constant for d-water.

4. DISCUSSION

SANS data from the CTVB/d-water ionic polymerized micelle system are characterized by varying features when the CTVB fraction increases. For low volume fractions, the MSA model developed for particulate systems with Coulomb interactions applies. A model consisting of the form factor for rodlike particles and the MSA structure factor was used to fit the SANS data. Fit results included rod dimensions (rod radius and length) in each case along with the macroion charge. This charge was found to be very small pointing to almost neutral rodlike particles.

REFERENCES

R.C. Weast, Editor-in-Chief, "CRC Handbook of Chemistry and Physics", 65th Edition, Page E57 (1884).

S.R. Kline, "Polymerization of Rodlike Micelles", Langmuir 15, 1726-1732 (1999)

T-H Kim, S-M Choi and S.R. Kline, “Polymerized Rodlike Nanoparticles with Controlled Surface Charge Density”, Langmuir 22, 2844-2850, (2006)

QUESTIONS

1. What is the form factor for an infinitely thin rod of length L?
2. Name two possible closure relations used to solve the Ornstein-Zernike equation for particulate systems?
3. What is the Debye-Huckel screening length? Define it for a neutral solution of macroions of charge $z_m e$ and electrons.
4. What is the CMC?
5. What is the radius of gyration for a cylindrical rod of radius R and length L?

ANSWERS

1. The form factor for an infinitely thin rod of length L is given by:

$$P(Q) = \frac{1}{2}\int_{-1}^{1} d\mu \left[\frac{\sin(Q\mu L/2)}{Q\mu L/2}\right]^2 .$$

2. Two possible closure relations used to solve the Ornstein-Zernike equation for particulate systems are: the Percus-Yevick and the Mean Spherical Approximation.
3. The Debye-Huckel screening length is the distance beyond which Coulomb interactions die out (are screened). The Debye-Huckel screening parameter (inverse length) is given by: $\kappa^2 = \frac{e^2}{k_B T} z_m \overline{N}$ where e is the electron charge, $z_m e$ is the macroion charge, $\overline{N}$ is the macroion number density (number per unit volume) and $k_B T$ is the sample temperature in absolute units.
4. The Critical Micelle Concentration (CMC) is the surfactant concentration for which micelles form.
5. The radius of gyration for a cylindrical rod of radius R and length L is given by:

$$R_g = \sqrt{\frac{R^2}{2} + \frac{L^2}{12}} .$$